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EUROPEAN PATENT APPLICATION

21 Application number: 89116424.6

51 Int. Cl.⁵: C08L 27/06 , C08L 33/00

22 Date of filing: 06.09.89

30 Priority: 09.09.88 US 242394
17.03.89 US 342800

43 Date of publication of application:
14.03.90 Bulletin 90/11

84 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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64 Polyvinyl chloride blends having improved physical properties.

57 Polyvinyl chloride-acrylate copolymers are plasticized with plasticizers to produce a composition having low hardness values. For example, Shore A values of 55 or less can be readily achieved. Such low values are often achieved by utilizing low amounts, for example less than 100 parts by weight, of the plasticizer for every 100 parts by weight of the PVC-acrylate copolymer. Low Shore A hardness values are also aided by the use of high amounts of acrylate units in the copolymer, that is amounts of at least 45 percent by weight based upon the total weight of the copolymer. The copolymer is made from a vinyl constituent which is a vinyl chloride monomer with an optional vinyl component comonomer and one or more acrylate monomers.

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POLYVINYL CHLORIDE BLENDS HAVING IMPROVED PHYSICAL PROPERTIES

FIELD OF THE INVENTION

5 The present invention relates to vinyl chloride-acrylate copolymer compositions having improved properties. More specifically, the present invention relates to polyvinyl chloride-acrylate copolymers which are blended with plasticizers which improve the flexibility and the low temperature brittleness thereby improving the physical properties. The properties which are improved include Shore A hardness as measured by ASTM D-2240, low temperature brittleness, as measured by ASTM D-746, tear properties, as measured by ASTM D-624, and oil swell in hot ASTM #3 oil at 100 °C for 166 hours as measured by ASTM
10 D-471.

BACKGROUND

15 Heretofore, plasticized polyvinyl chloride compositions generally did not have a Shore A hardness value of lower than from 55 to about 60. Further, flexible polyvinyl chloride compositions generally did not have favorable low temperature brittleness and good resistance to shrinkage in hot oil. The blends of the present invention achieve favorable low temperature brittleness, as well as other physical properties. These blends
20 can be utilized as gaskets, sealants, roofing membranes, shoe soles, liners for ponds, hoses, tarpaulins, and the like.

SUMMARY OF THE INVENTION

25 The plasticized polyvinyl chloride compositions of the present invention are very soft and flexible and have exceedingly low Shore A hardness values. The compositions have relatively low plasticizer migration and have good aging properties. These compositions are processable by a variety of techniques including injection molding, extrusion, calendering, thermoforming, and the like. The composition is a plasticized
30 polyvinyl chloride-acrylate copolymer. Moreover, the amount of the plasticizers generally utilized are usually low in comparison to conventional plasticized polyvinyl chloride compounds.

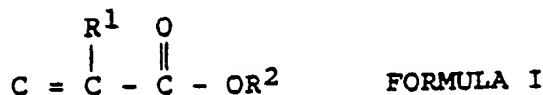
The flexible polyvinyl chloride compositions of the present invention also have improved brittleness properties, improved tear properties, and decreased oil swell in hot oil. The compositions are based on a
35 polyvinyl chloride-acrylate copolymer blended with low temperature property improving polymers.

DETAILED DESCRIPTION OF THE INVENTION

40 The flexible polyvinyl chloride compositions of the present invention contain polyvinyl chloride in the form of a copolymer. The copolymer is a polyvinyl chloride-acrylate copolymer made from (a) a vinyl chloride constituent, that is, a vinyl chloride monomer and an optional vinyl component comonomer and (b) one or more acrylate monomers. The amount of vinyl chloride monomer and optional vinyl component
45 comonomer utilized to make the polyvinyl chloride-acrylate copolymer is a sufficient amount so that the polyvinyl chloride-acrylate copolymer generally contains from about 10 parts to about 90 parts by weight, desirably from about 20 parts to about 75 parts by weight and preferably from about 30 parts to about 60 parts by weight of vinyl chloride and/or optional vinyl component units therein for every 100 parts by weight of the copolymer. Thus, the amount of the acrylate units in the copolymer is generally from about 90 parts
50 to about 10 parts by weight, desirably from about 80 to about 25 parts by weight, and preferably from about 70 to about 40 parts by weight. The amount of the optional vinyl component units in the copolymer is from about 0 to about 45 parts by weight with from about 0 to about 20 parts by weight being preferred. In other words, the vinyl chloride constituent can contain up to 50 percent thereof and preferably up to 22 percent thereof by weight of the vinyl component unit. By the term "vinyl component," it is meant a vinyl unit other than vinyl chloride. Such units are well known to the art and to the literature and are derived from vinyl

esters wherein the ester portion contains from 1 to 18 carbon atoms such as vinyl acetate; vinylidene chloride; 1,2-dichloroethylene; styrene and styrene derivatives having a total of from 8 to 15 carbon atoms such as alpha-methylstyrene, vinyl toluene, chlorostyrene, chloromethylstyrene; vinyl naphthalene; diolefins having a total of from 4 to 18 carbon atoms such as butadiene, isoprene, including halogenated diolefins such as chloroprene; monoolefins having a total of from 2 to 18 carbon atoms and preferably 2 to 4 carbon atoms; carbon monoxide, and the like. Vinyl acetate is a preferred vinyl component comonomer which, upon polymerization, becomes a vinyl component unit.

The one or more acrylate units contained in the polyvinyl chloride-acrylate copolymer have the formula, before polymerization,



wherein R¹ is an aromatic, an aliphatic (especially an alkyl), or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative thereof, desirably is methyl, and preferably is hydrogen. R² is an aliphatic group, especially an alkyl, an aromatic, a hydroxylalkyl, or combinations thereof, having from 1 to 18 carbon atoms, desirably from 2 to 10 carbon atoms, and Preferably from 2 to 8 carbon atoms, or a halogen derivative thereof; or R² is a hydrocarbyl ether such as an alkoxyalkyl, a phenoxyaryl, or a phenoxyalkyl, or combinations thereof having from 2 to 1,000 carbon atoms, desirably from 2 to 18 carbon atoms, and preferably from 2 to 8 carbon atoms, or a substituted halogen, oxygen, nitrogen, or sulfur derivative thereof. Examples of specific acrylate monomers include ethyl acrylate, propyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, 2-ethylhexyl acrylate, nonyl acrylate, decyl acrylate, phenyl acrylate, nonylphenyl acrylate, ethyl methacrylate, butyl methacrylate, hexyl methacrylate, 2-ethyl-hexyl methacrylate, lauryl methacrylate, methoxymethyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, butoxyethyl acrylate, ethoxypropyl acrylate, 2(2-ethoxyethoxy)ethyl acrylate, and the like. Especially preferred acrylate monomers include butyl acrylate, 2-ethyl-hexyl acrylate, ethyl acrylate, 2(2-ethoxyethoxy)-ethyl acrylate, and the like. As noted hereinabove, the R² group can be a hydrocarbyl ether group. That is, it can be an ether, a diether, or a multiple ether of an alkyl, an aryl, or combinations thereof, such as an alkoxyalkyl, a phenoxyaryl, a phenoxyalkyl, and the like, generally having from 2 to 1,000 carbon atoms, desirably from 2 to 18 carbon atoms, and preferably from 2 to 8 carbon atoms, or combinations thereof. Examples of specific alkoxyalkyl acrylates include methoxymethyl acrylate, butoxyethyl acrylate; ethoxypropyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, 2(2-ethoxyethoxy)ethylacrylate, and the like. Examples of specific phenoxyalkyl acrylates include 2-phenoxyethylacrylate and 2-phenoxyethylmethacrylate. In addition to the above R² ether groups, halogen, oxygen, nitrogen, or sulfur derivatives of such hydrocarbyl ether groups can also be utilized. For example R² can be an alkoxyalkyl containing at least one halogen therein in lieu of a hydrogen atom.

The molecular weight of the polyvinyl chloride-acrylate copolymer is measured in terms of inherent viscosity and is from about 0.3 to about 4.0, desirably from about 0.8 to about 2.5, and preferably from about 1.0 to about 2.2. The inherent viscosity is measured utilizing cyclohexanone as the solvent. It is noted that in some instances viscosity cannot be measured since the polymer will not fully dissolve. The copolymer is dissolved in the solvent at a concentration of 0.2 percent by weight at 90°C for 90 minutes and then the viscosity is measured with a viscometer in a water bath at 30°C.

The polyvinyl chloride-acrylate copolymer can be polymerized from the above-noted monomers in any conventional manner such as dispersion, emulsion, mass, solution, and the like with suspension being preferred. Generally, polymerization is initiated with a free radical initiator such as an alkanoyl, aroyl, alkaroyl, or an aralkanoyl diperoxide, a monohydroperoxide, or an azo compound, a peroxy ester, a percarbonate, or any other suitable free radical-type initiator. Examples of specific initiators include benzoyl peroxide, lauroyl peroxide, diacetyl peroxide, cumene hydroperoxides, methyl ethyl ketone peroxide, diisopropylbenzene hydroperoxide, 2,4-dichlorobenzoyl peroxide, naphthoyl peroxide, t-butyl perbenzoate, di-t-butyl perphthalate, isopropyl percarbonate, acetyl cyclohexane sulfonyl peroxide, disecundary butyl peroxydicarbonate, t-butyl peroxyneodecanoate, dinormal propyl peroxydicarbonate, azo-bis(isobutyronitrile), alpha, alpha-azodiisobutyrate, 2,2'-azo-bis-(2,4-dimethyl valeronitrile), and the like. Polymerization can be carried out at suitable temperatures with temperatures of from about 10° to 85°C being desired and from about 40° to about 65°C being preferred. The amount of the initiator utilized is generally quite small as from about 0.005 parts by weight to about 1.0 parts by weight and preferably from about 0.01 to about 0.1 parts by weight for

every 100 parts by weight of the total monomers being copolymerized.

The polyvinyl chloride-acrylate copolymer desirably is not crosslinked so that it has good processing properties. However, it is to be understood that it is within the ambit of the present invention to either partially crosslink or crosslink the polyvinyl chloride-acrylate copolymer to provide improved physical properties. Should the polyvinyl chloride-acrylate copolymer be crosslinked or cured, any conventional crosslinking agent can be utilized such as diallyl phthalate, various diacrylates such as butanediol diacrylate, diethylene glycol diacrylate, and the like.

According to the concepts of the present invention, very soft polyvinyl chloride compositions, that is, compositions containing polyvinyl chloride-acrylate copolymers, are achieved when plasticized with conventional plasticizers. Such plasticizers are generally well known to those skilled in the art as well as in the literature. Examples of suitable plasticizers for the above-noted polyvinyl chloride-acrylate copolymers include various adipic acid derivatives, azelaic acid derivatives, benzoic acid derivatives, citric acid derivatives, epoxy derivatives, ethers, formal derivatives, glycol derivatives, glycolates, glycerol derivatives, polyglycerol derivatives, petroleum derivatives, isobutyric acid derivatives, isophthalic acid derivatives, isosebacic acid derivatives, oleic acid derivatives, paraffin derivatives, pentaerythritol derivative, phosphoric acid derivatives, phthalic acid derivatives, ricinoleic acid derivatives, sebacic acid derivatives, stearic acid derivatives, sulfonamides and sulfonates, tartaric acid derivatives, terephthalates, trimellitates, various plasticizing type polymers such as various polyesters, nitrile-butadiene copolymers, chlorinated polyolefins, oxidized polyolefins, polyepichlorohydrins, polyacrylates, polysiloxanes, and the like, and combinations of the above. The above plasticizers as well as other plasticizers which can be utilized in the present invention include those set forth in The Technology of Plasticizers, by Sears and Darby, pages 893-1085, John Wiley & Sons, New York, 1982, which is hereby fully incorporated by reference.

Considering the adipic acid derivatives, they generally constitute a preferred class of plasticizing agents and are usually a diester, wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, with specific examples including diisobutyl adipate, di-2-ethylhexyl adipate (DOA), heptyl nonyladipate, octyl decyl adipate (n-octyl, n-decyl; NDODA-6,10), diisodecyl adipate (DIDA), dibutoxyethyl adipate, di(methylcyclohexyl) adipate, bis(2,2,4-trimethyl-1,3-pentanediolmono isobutyrate adipate, with di-2-ethylhexyl adipate being preferred.

The azelaic acid derivatives are generally diesters, wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, with specific examples including di-n-hexyl azelate, di-2-ethylbutyl azelate, and di-2-ethylhexyl azelate (DOZ).

The benzoic acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms, with specific examples including ethylene glycol dibenzoate, diethylene glycol dibenzoate, triethylene glycol dibenzoate, and polyethylene glycol (200) dibenzoate.

The various citric acid derivatives are generally triesters wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms in the ester portion, with specific examples including tri-n-butyl citrate, acetyl tri-n-butyl citrate, and acetyl tri(n-octyl, n-decyl) citrate.

Epoxy derivatives which are suitable in the present invention include epoxidized soybean oil, 2-ethylhexyl epoxy tallate, epoxidized propylene glycol dioleate, and Bisphenol A diglycidyl ether.

The ethers generally have a total of from about 2 to about 50 carbon atoms, with a specific example being o-nitrodiphenylether.

Dibutoxyethoxyethyl formal is a specific example of the various formal plasticizing agents which can have a total of from about 3 to about 40 carbon atoms.

The various glycol derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms. Suitable examples of glycol derivatives include diethylene glycol dipelargonate, triethylene glycol dipelargonate, triethylene glycol di-2-ethylbutyrate, triethylene glycol di-2-ethylhexoate, and polyethylene glycol (200) di-2-ethylhexoate.

The glycolates generally exist as aromatic esters or alkyl substituted aromatic esters wherein each alcohol group which forms the ester, independently, contains from 1 to 20 carbon atoms, with suitable examples including methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, and butyl phthalyl butyl glycolate.

The glycerol and polyglycerol derivatives generally exist as esters wherein each acid group which forms the ester, independently, contains from 1 to 18 carbon atoms, with specific examples including glyceryl monooleate, and glyceryl tributyrate.

Petroleum derivatives include various distillate fractions such as the terphenyls, the polyalkyl naphthalenes, white paraffin oil, and the like.

The various isobutyric acid derivatives are generally diesters wherein each alcohol group which forms

the ester, independently, contains from 1 to 18 carbon atoms with a specific example including 2,2,4-trimethyl-1,3-pentanediol diisobutyrate.

The various isophthalic acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with a specific example including di-2-ethylhexyl isophthalate.

The various isosebacic acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including di-n-butyl isosebacate and di-2-ethylhexyl isosebacate.

The various oleic acid derivatives are generally esters wherein each acid group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including butyl oleate.

The paraffins can be halogenated such as chlorinated. Suitable specific examples include chlorinated paraffin, 42 percent chlorine.

The pentaerythritol derivatives are generally esters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including pentaerythritol, fatty acid ester.

The various phosphoric acid derivatives are generally triesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including tributylphosphate, tri-2-ethylhexyl phosphate (TOF), tributoxyethyl phosphate, cresyl diphenyl phosphate (CDP), tricresyl phosphate (TCP), tridimethylphenyl phosphate: triphenyl phosphate, 2:3 with 2-ethylhexyl diphenyl phosphate: isopropylphenyl diphenylphosphate, t-butylphenyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, isodecyl diphenyl phosphate, and tris(2-chloroethyl) phosphate.

The various phthalic acid derivatives generally exist as a diester and constitute a preferred class of plasticizing agents. These derivatives generally exist as an ester wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms and specific examples include dibutylphthalate, diisohexyl phthalate, dimethylisobutylcarbonylphthalate, butyl octyl phthalate, butyl isodecylphthalate, di-n-octyl phthalate, di-2-ethylhexyl phthalate (DOP), diisooctyl Phthalate (DIOP), dicapryl phthalate, di(heptyl,nonyl) phthalate, di(heptyl,nonyl,undecyl)phthalate, diisononylphthalate, n-octyl n-decyl phthalate (DNODP-6,10), diisodecyl phthalate (DIDP), diundecyl phthalate (DUP), ditridecylphthalate (DTDP), diallyl phthalate, dihydroabietyl phthalate, butyl cyclohexylphthalate, butyl benzyl phthalate (Santicizer 160), alkyl benzyl phthalate (Santicizer 261), dicyclohexylphthalate (DCHP), diphenyl phthalate (DPP), alkyl aryl modified phthalate (Santicizer 213), dimethoxyethyl phthalate, diethoxyethoxyethyl phthalate, and dibutoxyethyl phthalate. Di-2-ethylhexyl phthalate is a highly preferred plasticizer.

The various ricinoleic acid derivatives are generally esters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including methyl ricinoleate, methyl acetyl ricinoleate, n-butyl acetyl ricinoleate, and methoxyethyl acetyl ricinoleate.

The sebacic acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with a specific example including di-2-ethylhexyl sebacate (DOS).

The various stearic acid derivatives are generally esters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including n-butyl stearate; butyl acetoxy stearate; methoxyethyl acetoxy stearate; and methyl pentachlorostearate.

The various sulfonamides and sulfonates are esters and amides of sulfonic acid, with specific examples including n-ethyl o,p-toluene sulfonamide, n-cyclohexyl p-toluene sulfonamide; and an alkyl sulfonic acid ester based on phenol and cresol.

The tartaric acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with a specific example being dibutyl tartrate.

The terephthalate acid derivatives are generally diesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with a specific example being di-2-ethylhexyl terephthalate.

The various trimellitate derivatives are generally triesters wherein each alcohol group which forms the ester, independently, contains from 1 to 18 carbon atoms with specific examples including tri-2-ethylhexyl trimellitate (TOTM), tri(heptyl, nonyl)trimellitate, n-octyl, n-decyl trimellitate, and triisodecyl trimellitate.

Homologs of the acid portion used to make the above plasticizers are also within the scope of the present invention.

Mineral oil is also a suitable plasticizer which can be utilized in the present invention. As known to those skilled in the art and to the literature, mineral oil is a purified petroleum product generally made from a fraction boiling between 330° and 390°.

The above plasticizers which are esters can also be a halogen, oxygen, sulfur, or a nitrogen derivative

thereof. That is, the alcohol group and/or the acid group which form the ester portion of the compound can have a halogen, oxygen, sulfur, or nitrogen substituent thereon.

As noted above, various polymers can be utilized as plasticizers. Polystyrene plasticizers include various polymers of styrene or derivatives thereof such as those having from 8 to 12 carbon atoms such as poly-alpha-methyl styrene, and the like.

Polyester plasticizers are generally made from a dicarboxylic acid having from about 2 to about 12 carbon atoms and from a diol having from about 2 to about 1,000 carbon atoms with propylene glycol being preferred. Examples of suitable polyesters include various esters made from adipic acid such as an ester having a molecular weight of 6,000, e.g., Paraplex G-40, a polyester made from adipic acid having a molecular weight of about 2,200 such as Paraplex G-50, a polyester made from adipic acid having a molecular weight of about 3,300 such as Paraplex G-54, a polyester made from azelaic acid having a molecular weight of about 2,200 such as Plastolein 975, a polyester made from sebacic acid such as Paraplex G-25, a polyester made from glutaric acid, a polycaprolactone polyester, and the like. Paraplex is a trademark of C. P. Hall and Plastolein is a trademark of Emery Industries, Inc.

Various nitrile-butadiene copolymers can be utilized which are generally soft. In order to achieve such soft copolymers, the nitrile content is generally 50 percent by weight or less and preferably 40 percent by weight or less.

The chlorinated polyolefins are made from olefin monomers having from 1 to 18 carbon atoms and generally have a chlorine content of 50 percent by weight or less and desirably 45 percent by weight or less. The oxidized polyolefins are also made from olefin monomers having from 1 to 18 carbon atoms.

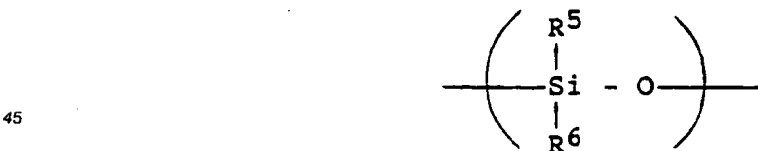
Various polyepichlorohydrin polymers or copolymers, that is polyethers, can be utilized and such generally have a weight average molecular weight of from about 100,000 to about 1,000,000.

The polyacrylates which are utilized as plasticizers are very soft compounds and thus generally have a weight average molecular weight of 100,000 or less. Such polymers are made from monomers having the formula



wherein R^3 is an aromatic, an aliphatic such as an alkyl, or combinations having from 1 to 18 carbon atoms, or a halogen derivative thereof, but desirably is methyl and preferably is hydrogen. The R^4 group is an aliphatic such as an alkyl, an aromatic, an alkyl hydroxyl, or combinations thereof, having from 1 to 18 carbon atoms, desirably from 2 to 8 carbon atoms, or a halogen derivative of the above; or a hydrocarbonyl ether such as an alkoxyalkyl, a phenoxyaryl, or a phenoxyalkyl, or combinations thereof, having from 2 to 1,000 carbon atoms, desirably from 2 to 8 carbon atoms, or as a substituted halogen, oxygen, nitrogen, or a sulfur derivative thereof.

The various polysiloxane plasticizers generally have



as a repeat unit wherein R^5 and R^6 , independently, is an aliphatic or an aromatic having from 1 to 18 carbon atoms.

The plasticized polyvinyl chloride acrylate copolymer blends of the present invention have unexpectedly been found to be very soft, that is have very low Shore A values. Moreover, migration, that is bleed-out of the plasticizer, is generally very low or non-existent. The amounts of plasticizer utilized generally range from about 0 to about 300 parts by weight, desirably from about 2 to about 100 parts by weight and preferably from about 5 or 10 to about 50 parts by weight for every 100 parts by weight of the polyvinyl chloride-acrylate copolymer. According to the concepts of the present invention, it has also been found that if high amounts of acrylate units are contained in the polyvinyl chloride-acrylate copolymer such as at least 45 parts by weight and desirably at least 55 parts by weight, a plasticizer need not always be utilized to

achieve a soft polyvinyl chloride-acrylate composition.

Generally, plasticizers which are preferred in the present invention include the various adipates, the various phthalates, the various trimellitates, the various copolymers of nitrile-butadiene, the various formals, the various polyesters, and mineral oil and the various polysiloxanes.

5 Heretofore the lowest Shore A hardness values which could be reasonably obtained with plasticized polyvinyl chloride polymers was generally from about 55 to about 60. However, in accordance with the present invention, effective amounts of plasticizers can be utilized to achieve a Shore A hardness value of about 55 or less, desirably 50 or less, preferably 40 or less, and even 30 or less. Naturally, the amount of plasticizer which is utilized will tend to vary with the type of acrylate comonomer utilized to form the
10 copolymer, the amount of the acrylate comonomer, the type of the plasticizer, and the like. However, as noted above, such amounts are generally low in comparison with conventionally plasticized PVC compounds, and when high amounts of acrylate units are utilized in the polyvinyl chloride-acrylate copolymer, the use of a plasticizer can be, at times, completely eliminated.

Other properties according to the first embodiment of the present invention include the achievement of
15 improved low temperature properties, that is low brittleness temperature as measured by ASTM D-746. Generally, brittleness temperatures of minus 35°C or less, desirably minus 40°C or less, and preferably minus 50°C or less (i.e., colder) are produced. Percent oil swell is also lowered and improved flex modulus, that is a lower flex modulus number, is achieved. According to the present invention, low temperature Clash-Berg modulus are also improved and are generally 50,000 psi or less, desirably 20,000 psi or less,
20 and preferably 10,000 psi or less when measured in accordance with ASTM D-1043 at -35°C.

The plasticized polyvinyl chloride-acrylate copolymers of the present invention can also contain conventional additives in conventional amounts. Thus, various heat stabilizers such as barium/cadmium compounds, lead compounds, and organotin compounds, various conventional lubricants such as paraffin, polyethylene, stearic acid, various processing aids such as polyacrylates, various antioxidants such as BHT,
25 that is butylated hydroxy toluene, BHA, that is butylated hydroxy anisole, various hindered phenols, various UV inhibitors such as substituted benzophenones, and the like, can be utilized.

Various fillers and pigments can also be utilized in conventional amounts such as up to about 200 or 300 parts by weight for every 100 parts by weight of the polyvinyl chloride-acrylate copolymer. Examples of fillers include calcium carbonate, clay, silica, the various silicates, talc, carbon black, and the like. Such
30 fillers are generally added in high amounts as from about 10 to about 200 parts by weight for every 100 parts by weight of the polyvinyl chloride-acrylate copolymer. Examples of various pigments include titanium dioxide, carbon black, and the like. Generally, the amount of such pigment is not as large as the amount of the fillers.

The various additives, fillers, pigments, and the like, are generally added and blended in any
35 conventional manner. For example, the polyvinyl chloride-acrylate copolymer can be blended with the various additives in a Banbury mixer and then processed on a two-roll mill to produce a sheet which can be cubed and then extruded, injection molded, etc. The polyvinyl chloride-acrylate copolymer can also be mixed with the various additives in a high intensity mixer such as a Henschel mixer and then this powder compound can be processed on a two-roll mill into a sheet and cubed or the powder compound can be
40 processed on an extruder into pellets or into the finished article. In general, any conventional compounding equipment such as a Banbury mixer, two-roll mill, extruder, injection molding machine, etc., can be used to produce the products of this invention.

Regardless of the particular blending technique or operation utilized, an important processing advantage of the present invention is that the various components can be processed on conventional elastomer
45 equipment. Examples of conventional elastomer equipment include mills, mixers, and extruders designed for the processing of elastomers. Such equipment is generally heated and/or cooled. The extruders usually have a length/diameter ratio of 20 or less.

The plasticized polyvinyl chloride-acrylate copolymers of the present invention can be utilized to produce very soft products with the addition of very little plasticizer. The plasticized copolymer containing
50 the various fillers, additives, etc., can be processed by a variety of techniques including injection molding, extrusion, calendering, thermoforming, and the like. Suitable end use applications include caulks, sealants, gaskets such as automotive gaskets, fishing lures, fabric reinforcement, hot melt adhesives, and the like.

According to another embodiment, the polyvinyl chloride-acrylate copolymers are blended with low temperature brittleness improving polymers which are non-liquid and high molecular weight. These
55 polymers are physically blended with the polyvinyl chloride-acrylate copolymers to produce a generally homogeneous and compatible blend. The term "low temperature property improving polymers" is used as a generic description of the polymers blended with the polyvinyl chloride-acrylate copolymers of the present invention. These polymers are generally thermoplastic, i.e. are processable on thermoplastic

equipment, and have a high weight average molecular weight, i.e. greater than 5,000, and preferably greater than 10,000. The resultant blends have good low temperature brittleness properties of less than -10°C , and preferably less than -20°C , as measured by ASTM D746. The blends have a Shore A hardness value of less than or equal to about 90, and preferably less than or equal to 85 as measured by ASTM D-2240. The blends also display an oil swell in hot ASTM #3 oil at 100°C for 166 hours of from about 0 percent to about 300 percent, and preferably from about 0 percent to about 200 percent. Tear resistance is also improved and is greater than 30 lbs/in, preferably greater than 50 lbs/in, and most preferably greater than 100 lbs/in, as measured by ASTM D-624 die C. Broadly speaking, the following classes of polymers are suitable: polyester elastomers, polyurethanes, thermoplastic rubbers, and ethylene homopolymer or copolymers.

These can be used separately or in combination.

Suitable polyester elastomers include those commercially available under the trade name of "Hytrel", manufactured by E.I. DuPont DeNemours, Inc. and under the tradename of "Lomod" manufactured by General Electric, Inc. The polyesters are generally the condensation polymerization product of a polyether diol or polyol with a dicarboxylic acid. The weight average molecular weight of suitable polyester elastomers is generally greater than 5,000, and desirably greater than 10,000. Most preferably, suitable polyester elastomers have a Shore D hardness ASTM D2240, of less than about 50. A description of such elastomers is found in Thermoplastic Elastomers by N. L. Legge, G. Holden and H. E. Schroeder, pp. 163-196, Hansen Publishers, Munich, 1987, and Handbook of Thermoplastic Elastomers by B. Walker, pp. 103-215, Krieger Publishing, Melbourne, Florida, 1986, which are fully incorporated by reference.

Polyurethanes which are suitable include those made from an intermediate generally made from a polyester or polyether polyol and may contain a low molecular weight diol chain extender. The intermediate generally has a weight average molecular weight of greater than 500. The intermediate is reacted with a polyisocyanate having a formula $(\text{RNCO})_n$, wherein R is an aliphatic or an aromatic, or combinations thereof. The subscript "n" can generally be an integer of from 2 to about 4, with 2 being preferred. Inasmuch as the low temperature brittleness improving polymers are thermoplastic, the polyurethanes are not highly crosslinked with a curing agent. Slight or partial crosslinking can occur but to a limited amount in that the urethane polymer must be flexible. A description of such polyurethanes can be found in Thermoplastic Elastomers, pp. 13-46 and Handbook of Thermoplastic Elastomers, pp. 216-246. Such polyurethanes can be extrusion grade, injection molding grade, and calendering grade. Specific examples of suitable extrusion grade polyurethanes include those having a melt index of 5 to 50 grams per 10 minutes measured from 190 to 210°C with a load of 1200-8700 grams. Preferably, the polyurethane has a Shore D hardness, ASTM D2240, of less than about 50.

The thermoplastic rubbers or elastomers of the present invention are not cured or only cured to a limited or partial extent. The terms "elastomer" and "rubber" are used interchangeably herein. Suitable elastomers or rubbers include natural rubber; ethylene-propylene rubber; derivatives of polyethylene such as "Hypalon" from E.I. DuPont de Nemours, Inc.; ethylene-propylene-diene rubber; rubbers made from conjugated dienes having from 4 to 12 carbon atoms, and preferably from 4 to 8 carbon atoms; butyl and halogenated butyl elastomers; silicone elastomers; fluorocarbon elastomers; rubbers made from such conjugated dienes and vinyl substituted aromatics having from 8 to 12 carbon atoms; elastomers prepared from halogenated diolefins such as polychloroprene; thermoplastic elastomers; and block or graft copolymers and overpolymers. Suitable rubbers include those described in Rubber Technology, by M. Morton, Van Nostrand Reinhold Company, New York, 1987, which is fully incorporated herein by reference. Preferred elastomers include ethylene-propylene rubber; ethylene-propylene-diene rubber; butyl rubber such as polyisobutylene polymerized with isoprene; styrene-butadiene rubber; polybutadiene; polyisoprene; natural rubber; silicone elastomers; elastomers prepared from halogenated diolefins, for example polychloroprene; styrene conjugated diene block copolymers including inter alia "Kraton" from Shell, Inc.; thermoplastic elastomers and dynamically vulcanized thermoplastic elastomers such as "Santoprene", sold by Monsanto Inc.; graft copolymers and/or overpolymers of styrene, methyl styrene, methacrylate, methyl-methacrylate, and acrylonitrile on elastomeric materials. Suitable examples of such graft copolymers and/or overpolymers include acrylonitrile-butadiene-styrene, methylmethacrylate-butadiene-styrene, methacrylate-butadiene-styrene, acrylonitrile-styrene-acrylate, methylmethacrylate-acrylate rubber, and methacrylate-acrylate rubber, acrylonitrile-styrene-chlorinated polyethylene, methacrylate-acrylonitrile-butadiene-styrene, acrylonitrile-methyl styrene-butadiene-styrene, and the like, or combinations thereof. Typical examples would include BTA 733 from Rohm and Haas, Inc.; Blendex 338 from General Electric, Inc.; and Durastrength 200 from M&T Chemicals, Inc. The weight average molecular weight of such elastomers or rubbers is generally in excess of 15,000 and preferably in excess of 50,000, and most preferably in excess of 100,000. In examples where there is significant crosslinking, the weight average molecular weight will, of course, be higher values. These elastomers may have the additional benefit of improving compression set.

Suitable ethylene-based polymers include copolymers of ethylene with 1) vinyl esters having from 1 to 18 carbon atoms in the acid portion used to make the ester, with vinyl acetate being preferred; 2) acrylates, wherein the acrylate has from 1 to 18 carbon atoms in the alcohol portion used to make the acrylate; and 3) monoolefins having from 2 to 18 carbon atoms, with from 2 to 8 carbon atoms being preferred and low density polyethylene. Combinations of the foregoing can be used. A further suitable ethylene based polymer is a terpolymer made from ethylene, vinyl esters, and carbon monoxide. Preferable ethylene copolymers include a copolymer of ethylene with one or more of (1) vinyl acetate; (2) acrylate esters, wherein the alcohol portion used to make the ester has from 1 to 4 carbon atoms; (3) monoolefins having from 2 to 8 carbon atoms; and (4) carbon monoxide. Most preferably the ethylene copolymer is selected from the group consisting of ethylene-vinyl acetate-carbon monoxide, ethylene-vinyl acetate, ethylene-ethylacrylate, and ethylene-methylacrylate. The weight average molecular weight of the ethylene polymers is generally in excess of 10,000 and preferably in excess of 50,000, and most preferably in excess of 100,000. The ethylene content in the copolymers should be greater than 20 percent, preferably greater than 40 percent, and most preferably greater than 50 percent.

The invention will be better understood by reference to the following examples.

EXAMPLE 1

Procedure of vinyl chloride monomer/2-ethylhexyl acrylate polymerization.
The polymerization vessel was charged with the following ingredients:

Water	2223 kg.
Vinylchloride monomer	889 kg.
2-ethylhexyl acrylate	593 kg.
Polyvinyl alcohol dispersants	28.2 kg.
Substituted cellulose dispersant	22.7 kg.
Initiator	0.445 kg.

The vessel was charged with water and the dispersants first. After evacuation, the mixture of monomers was added and after the mixing of the contents, the temperature was adjusted to 55° C. Lastly, the initiator was added and the reaction started. The polymerization was carried out with agitation for 420 minutes after which time the reactor was cooled to room temperature. The polymer slurry was transferred to a stripping vessel to remove unreacted monomers. After the stripping, the polymer was recovered by filtration and dried.

EXAMPLE 2

Using a resin similar to that given in Example 1, the blends listed in Table I were prepared. The blends using the polyvinyl chloride-acrylate copolymer were prepared by mixing the ingredients on a heated 6" x 13" two-roll mill with a mill temperature of 149° C for 8 minutes after banding. The product was then removed as a sheet from the mill and cut into 6" x 6" plaques. The plaques were pressed using a two minute preheat and three minute press time at 160° C. The pressed plaques were then submitted for physical testing. The polyvinyl chloride homopolymer compounds were prepared in a similar fashion except that the mill temperature was 160° C for the compound containing 90 PHR of plasticizer, 146° C for the compound containing 100 PHR of plasticizer and these compounds were milled for 5 minutes and 10 minutes after banding, respectively. These compounds were then pressed using a 5 minute preheat and a 5 minute press time at 177° C.

The results in Table I indicate that plasticizers can be added to the polyvinyl chloride-acrylate copolymer to produce products with lower hardness values, better low temperature properties and, depending on the plasticizer chosen, reduced oil swell. These products can have significantly lower hardness values (depending on the level of plasticizer used) than polyvinyl chloride homopolymer resins containing very high levels of a typical polyvinyl chloride plasticizer. Also, plasticizers not typically usable to

plasticize polyvinyl chloride homopolymers (silicone fluid and mineral oil) can be used to plasticize the polyvinyl chloride-acrylate copolymers.

TABLE I

PVC Homopolymer Resin (1.02 Inherent Viscosity)	100 ¹	100 ²	-	-	-
Di-2-ethylhexyl Phthalate	90	100	-	-	-
PVC/2-ethylhexyl acrylate copolymer	-	-	100 ¹	100 ¹	100 ¹
Silicone Fluid - SF 1265*	-	-	-	5	10
Mineral Oil - USP White	-	-	-	-	-
Hardness - Shore A ASTM D-2240	64	56	62	58	52
Brittleness Temperature (°C) ASTM D-746	-45.5	-48	-22.5	-25.0	-27.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	5000	2600	53350	40300	23500
Oil Resistance - % Volume Swell ASTM D-471, ASTM #3 Oil - 100°C/166 hrs.	-33	-54	176	174	178

* SF 1265 is manufactured by General Electric.

1 Compound also contains - stabilizer 5, co-stabilizer 3, filler 8 and lubricant 0.5. Ingredients added in parts per hundred resin unless otherwise indicated.

2 Compound also contains - stabilizer 2, co-stabilizer 10, lubricant 0.2

TABLE I (continued)

PVC Homopolymer Resin (1.02 Inherent Viscosity)	-	-	-	-
Di-2-ethylhexyl Phthalate	-	-	-	-
PVC/2-ethylhexyl acrylate copolymer	100 ¹	100 ¹	100 ¹	100 ¹
Silicone Fluid - SF 1265*	20	-	-	-
Mineral Oil - USP White	-	5	10	20
Hardness - Shore A ASTM D-2240	44	55	47	38
Brittleness Temperature (°C) ASTM D-746	-30.5	-30.0	-30.5	-32.0
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	21450	22600	13400	10750
Oil Resistance - % Volume/ Swell ASTM D-471, ASTM #3 Oil - 100°C/166 hrs.	185	170	162	164

* SF 1265 is manufactured by General Electric.

1 Compound also contains - stabilizer 5, co-stabilizer 3, filler 8 and lubricant 0.5. Ingredients added in parts per hundred resin unless otherwise indicated.

EXAMPLE 3

A resin similar to that described in Example 1 was blended with the ingredients listed in Table II using a laboratory size (BR size) Banbury mixer. The materials were dropped from the Banbury at the stock temperatures indicated in Table II and placed on a 6" x 16" unheated mill and formed into a sheet. The sheet was cut into both 1" wide strips and 6" x 6" plaques. The 1" wide strips were extruded on an extruder designed for processing elastomeric materials. The extruder was equipped with an approximately 7:1 length/diameter deep-flighted screw and was heated using circulating hot water. The samples were extruded using a Garvey die and the extrusion rates and stock temperatures during extrusion are given in Table II. The 6" x 6" plaques were pressed using a two-minute preheat and three minute press time at

160° C. The samples were then submitted for physical testing.

The results in Table II indicate that a plasticizer typically used for polyvinyl chloride homopolymer (di-2-ethylhexyl adipate) and one used for elastomeric materials (dibutoxyethoxyethyl formal) will both effectively plasticize the polyvinyl chloride/2-ethylhexyl acrylate copolymer. The results indicate that products are obtained which have low hardness values, improved low temperature properties and lower percent volume swell when tested in an oil immersion test. Also, the data in Table II demonstrates that these effects are seen with both an organic (carbon black) and an inorganic filler system.

TABLE II¹

PVC/2-ethylhexyl acrylate copolymer	100	100	100	100	100
Di-2-ethylhexyl adipate	-	-	5	10	20
Dibutoxyethoxyethyl formal	-	-	-	-	-
Calcium carbonate - 3.5% uncoated	50	50	50	50	50
Carbon black - N550 grade	-	-	-	-	-
Banbury Stock Temperature (°F)	302	284	297	290	282
Extrusion Stock Temperature (°F)	217	212	195	200	155
Extrusion rate (g/min.)	256	226	220	156	218
Hardness - Shore A ASTM D-2240	64	53	50	37	15
Brittleness Temperature (°C) ASTM D-746	-24	-36.5	-37.5	-45	-59.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	85150	36000	21250	1550	*
Oil Resistance - % Volume Swell ASTM D-471, ASTM #3 Oil - 100°C/166 hours.	234	243	219	192	152

¹Compounds also contain - stabilizer 5, co-stabilizer 3, lubricant 0.75 and antioxidant 0.5. Ingredients added in parts per hundred resin unless otherwise indicated.

*value was too low to be recorded by test apparatus.

TABLE III (continued)

PVC/2-ethylhexyl acrylate copolymer	100	100	100	100	100	100
Di-2-ethylhexyl adipate	-	-	-	-	5	10
Dibutoxyethoxyethyl formal	10	20	-	-	-	-
Calcium carbonate - 3.5% uncoated	50	50	-	-	-	-
Carbon black - N550 grade	-	-	20	20	20	20
Banbury Stock Temperature (°F)	307	293	327	324	315	315
Extrusion Stock Temperature (°F)	207	200	217	215	212	212
Extrusion rate (g/min.)	180	200	212	198	172	172
Hardness - Shore A ASTM D-2240	45	34	75	68	60	60
Brittleness Temperature (°C) ASTM D-746	-37.5	-46	-28	-28.5	-36	-36
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	10900	1100	73300	32250	11050	11050
Oil Resistance - % Volume Swell	206	185	183	166	163	163
ASTM D-471, ASTM #3 Oil - 100°C/166 hours.						

1 Compounds also contain - stabilizer 5, co-stabilizer 3, lubricant 0.75 and antioxidant 0.5. Ingredients added in parts per hundred resin unless otherwise indicated.

*Value was too low to be recorded by test apparatus.

TABLE III (continued)

PVC/2-ethylhexyl acrylate copolymer	100	100	100	100
Di-2-ethylhexyl adipate	20	50	-	-
Dibutoxyethoxyethyl formal	-	-	10	20
Calcium carbonate - 3.5% uncoated	-	-	-	-
Carbon black - N550 grade	20	20	20	20
Banbury Stock Temperature (°F)	306	286	310	317
Extrusion Stock Temperature (°F)	208	192	214	200
Extrusion rate (g/min.)	128	222	174	188
Hardness - Shore A ASTM D-2240	47	23	60	44
Brittleness Temperature (°C) ASTM D-746	-42.5	-61	-36.5	-42.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	1750	*	15700	1500
Oil Resistance - % Volume Swell ASTM D-471, ASTM #3 Oil - 100°C/166 hours.	153	115	169	166

*Compounds also contain - stabilizer 5, co-stabilizer 3, lubricant 0.75 and antioxidant 0.5. Ingredients added in parts per hundred resin unless otherwise indicated.

*Value was too low to be recorded by test apparatus.

EXAMPLE 4

A second lot of resin similar to that used in Example 3 was compounded with various levels of di-2-ethylhexyl phthalate plasticizer. These compounds were processed in the same manner as given in Example 3. A second sample of polyvinyl chloride/acrylate resin was compounded similar to the above and then extruded as in Example 3. The results of the physical testing and extrusions are given in Table III.

The results in Table III indicate that di-2-ethylhexyl phthalate will significantly soften the PVC/2-ethylhexyl acrylate copolymer even when used at relatively low levels. These compounds also show improved low temperature brittleness and lower Clash-Berg modulus values versus the PVC/2-ethylhexyl acrylate copolymer which contains no di-2-ethylhexyl phthalate.

TABLE III¹

PVC/2-ethylhexyl acrylate copolymer	100	100	100	100	100
Di-2-ethylhexyl phthalate	--	5	10	20	50
Calcium Carbonate - 3.5% Uncoated	50	50	50	50	50
Banbury Stock Temperature (°F)	327	314	298	301	310
Extrusion Stock Temperature (°F)	213	207	208	210	195
Extrusion Rate (g/min)	280	271	266	268	216
Hardness - Shore A	64	59	53	43	22
Brittleness Temperature (°C) ASTM D-746	-25.5	-26.5	-29.0	-34.0	-46.0
Clash-Berg Modulus at -35°C (psi)	76300	52700	36200	12400	700

1. Compounds also contain stabilizer 5, costabilizer 3, lubricant 0.75 and antioxidant 0.5

EXAMPLE 5

The polymerization vessel was charged with the following ingredients:

Water	2085 g.
Vinyl chloride monomer	685 g.
2-ethylhexyl acrylate	456 g.
Polyvinyl alcohol dispersant #1	25.2 g. of 6.4% water solution
Polyvinyl alcohol dispersant #2	24.2 g. of 2.8% water solution
Substituted cellulose dispersant	35.3 g. of 2.3% water solution
Initiator	0.58 g.

10

The vessel was first charged with water and then followed by the dispersants. After evacuation, the mixture of monomers was added and after the mixing of the contents, the temperature was adjusted to 55° C with constant agitation. Lastly, the initiator was added and the reaction started. The polymerization was carried out for 420 minutes, after which time, the reactor was cooled to room temperature. The polymer was transferred to a stripping vessel to remove unreacted monomers. After stripping, the polymer was recovered by filtration and drying. About 912 grams of polymer was obtained in the form of a white powder.

EXAMPLE 6

20

The polymerization vessel was charged with the following ingredients:

Water	2085 g.
Vinyl chloride monomer	685 g.
2-ethylhexyl acrylate	456 g.
Polyvinyl alcohol dispersant #1	25.2 g. of 6.4% water solution
Polyvinyl alcohol dispersant #2	24.2 g. of 2.8% water solution
Substituted cellulose dispersant	35.3 g. of 2.3% water solution
Initiator	0.84 g.

The vessel was first charged with water and then followed by the dispersants. After evacuation, the mixture of monomers was added and after the mixing of the contents, the temperature was adjusted to 45° C with constant agitation. Lastly, the initiator was added and the reaction started. The polymerization was carried out for 660 minutes, after which time, the reactor was cooled to room temperature. The polymer was transferred to a stripping vessel to remove unreacted monomers. After stripping, the polymer was recovered by filtration and drying. About 780 grams of polymer was obtained in the form of a white rubbery powder.

EXAMPLE 7

45

The polymerization vessel was charged with the following ingredients:

Water	1620 g.
Vinyl chloride monomer #1	540 g.
Vinyl chloride monomer #2	108 g.
2-ethylhexyl acrylate #1	378 g.
2-ethylhexyl acrylate #2	162 g.
Polyvinyl alcohol dispersant #1	25.2 g. of 6.4% water solution
Polyvinyl alcohol dispersant #2	24.2 g. of 2.8% water solution
Substituted cellulose dispersant	35.3 g. of 2.3% water solution
Initiator	0.95 g.

The vessel was first charged with water and then followed by the dispersants. After evacuation, the mixture of 2-ethylhexyl acrylate #1 and vinyl chloride monomer #1 was added and after the mixing of the contents, the temperature was adjusted to 45°C with constant agitation. Lastly, the initiator was added and the reaction started. Then 2-ethylhexyl acrylate #2 was metered during the first half of the reaction. Vinyl chloride monomer #2 was added near the end of the reaction. The polymerization was carried out for 720 minutes, after which time the reactor was cooled to room temperature. The polymer was transferred to a stripping vessel to remove unreacted monomers. After stripping, the polymer was recovered by filtration and drying. About 785 grams of polymer was obtained in the form of a white rubbery powder.

The resins from Examples 5, 6 and 7 were compounded in a manner and under conditions similar to Example II using a 6" x 13" two roll mill. Samples were removed as a sheet from the mill and cut into 6" x 6" plaques. The plaques were pressed in a manner as set forth in Example II and tested. The results of this testing are given in Table IV.

The results of Table IV indicate that products with low Shore A hardness values, good low temperature brittleness values according to ASTM D746, and low Clash-Berg modulus can be achieved without the addition of a plasticizer.

TABLE IV¹

Example	5	6	7
VCM/2-EHA ratio in copolymer	49.5/50.5	41.6/58.4	32.8/67.2
Polymerization Temperature (°C)	55	45	45
Hardness (Shore A)	60	48	38
Tensile Strength (psi)	1220	845	1130
Elongation (%)	300	575	653
Clash-Berg Modulus (psi) (0-35°C)	57830	26530	16995
Brittleness Temperature (°C) ASTM D746	-26.5	-33.5	-40.5

¹Compounds also contain stabilizer 5, costabilizer 3, filler 8, lubricant 0.5, and antioxidant 0.5.

EXAMPLE 8

The polymerization vessel was charged with the following ingredients in the order as given in the text below:

Water	26.67 kg
Vinyl chloride monomer #1	8.99 kg
Vinyl chloride monomer #2	2.7 kg
2-ethylhexyl acrylate #1	6.07 kg
n-butyl acrylate #1	0.674 kg
2-ethylhexyl acrylate #2	2.02 kg
n-butyl acrylate #2	0.225 kg
Polyvinyl alcohol dispersant #1	390 g. of 5.0% water solution
Polyvinyl alcohol dispersant #2	170 g. of 5.3% water solution
Substituted cellulose dispersant	550 g. of 2.3% water solution
Initiator	14.4 g.

The vessel was first charged with water and then followed by the dispersants. After evacuation, the mixture of 2-ethylhexyl acrylate #1, n-butyl acrylate #1, and vinyl chloride monomer #1 was added and after the mixing of the contents, the temperature was adjusted to 50° C with constant agitation. Lastly, the initiator was added and the reaction started. Then a mixture of 2-ethylhexyl acrylate #2 and n-butyl acrylate #2 was metered during the first half of the reaction. Vinyl chloride monomer #2 was metered near the end of the reaction. The polymerization was carried out for 540 minutes, after which time the reactor was cooled to room temperature. The polymer slurry was transferred to a stripping vessel to remove unreacted monomers. After stripping, the polymer was recovered by filtration and drying. About 14.6 kilograms (32.2 lbs) of polymer was obtained in the form of a white rubbery powder.

The resin from Example 8 was compounded in a manner and under conditions similar to the polyvinyl chloride acrylate copolymer based compound in Example 2 using a 6" x 13" two-roll mill. Samples were removed as a sheet from the mill and cut into 6" x 6" plaques. The plaques were pressed in a manner as set forth in Example 2 and tested. The results of this testing are given in Table V.

The results in Table V indicate that products with low Shore A hardness values, good low temperature brittleness values according to ASTM D746, and relatively low Clash-Berg moduli according to ASTM D-1043 can be achieved without the addition of a plasticizer. The addition of a relatively small amount of plasticizer results in a significant reduction in Clash-Berg modulus and Shore A hardness.

TABLE VI

Resin Example 8
with 2.5 phr of DIDP

Hardness (Shore A) ASTM D-2240	48	44
Tensile Strength (psi) ASTM D-412	750	590
Elongation (%) ASTM D-412	430	500
Clash-Berg Modulus (psi) at -35°C ASTM D-1043	67700	52000
Brittleness Temperature (°C) ASTM D-746	-30	-31
Compression Set (%) ASTM D-395 Method B (22 Hrs., 100°C)	45	44
(22 Hrs., RT)	40	41

1 Compounds also contain - tin stabilizer 1.8, co-stabilizer 0.25, lubricants 1.5, and antioxidant 0.2 phr. Ingredients added in parts per hundred resin unless otherwise indicated.

DIDP = Diisodecyl phthalate

EXAMPLE 9

The blends listed in Table VI were prepared using a resin similar to that described in Example 1. These blends were prepared on a heated 6" x 13" two-roll mill with a roll temperature of 160°C. The blends were milled for 2 minutes after banding and then removed as sheets from the mill. The sheets were cut into 6" x 6" plaques and compression molded. The compression molded plaques were then submitted for physical

testing.

The results in Table VI indicate that enhanced low temperature brittleness properties, tear strengths and lower volume swell in hot oil can be obtained by adding a polymeric additive (polyester elastomer) to a polyvinyl chloride-acrylate copolymer.

TABLE VI¹

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100
Polyester Elastomer (Hytrel 4056) ²	-	1.0	5.0	10.0	20	72
Hardness - Shore A ASTM D-2240	58	62	64	66	66	72
Brittleness Temp. (°C) ASTM D-746	-30.5	-30.5	-34.0	-34.5	-32.5	-32.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	65,300	63,500	60,200	74,450	72,150	72,150
Oil Resistance - Volume Swell, ASTM D-471, ASTM D 3 Oil 100°C/166 Hrs.	177	175	166	145	122	122
Tear Strength (PPI) ASTM D-624, die C	103	100	120	130	157	157

¹Compounds also contain - stabilizer 5, co-stabilizer 3, filler 8, antioxidant 0.5, and lubricant 0.75. Ingredients are added in parts per hundred resin unless otherwise indicated.

²E.I. DuPont de Nemours, Inc.

EXAMPLE 10

Using a resin similar to that given in Example 1, the blends listed in Tables VII, VIII, and IX were

prepared. These blends were prepared by mixing the ingredients on a heated 6" x 13" two-roll mill with a roll temperature of 149 to 199 °C depending on the substrate being blended. The blends were milled for 8 minutes after banding and the products were then removed as sheets from the mill and cut into 6" x 6" plaques. The plaques were pressed at 160 °C using a two minute preheat and a three minute press cycle.

5 The pressed plaques were then submitted for physical testing.

The results in Tables VII, VIII and IX indicate that a polyurethane as well as two different types of ethylene copolymers can be added to a polyvinyl chloride-acrylate copolymer in the presence of a standard plasticizer and give products with enhanced low temperature brittleness properties, tear strengths and, depending on the polymeric additive selected, lower volume swell values when immersed in hot oil.

TABLE VII

PVC/2-Ethylhexyl Acrylate Copolymer	100 ¹	100 ¹	100 ¹	100 ¹	100 ¹
Thermoplastic Polyurethane (Melt Index 5-17 g/10 min. at 210°C, 3800 g. load)	--	10	20	50	100
Chlorinated Polyethylene	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5
Hardness - Shore A ASTM D-2240	78	83	82	81	80
Brittleness Temp. (°C) ASTM D-746	-13.5	-11.5	-15	-20	-29.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	92,550	103,650	93,900	75,400	60,000
Oil Resistance - Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	141	118	124	96	69
Tear Strength (PPI) ASTM D-624, die C	150	190	165	190	220

1 Compound also contains - stabilizer and lubricants 7.9, fire retardant
gand antioxidant 3.45, filler 35, pigment and fungicide 16. Ingredients
are added in parts per hundred resin unless otherwise indicated.

TABLE VII (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	1002	1002	1002	1002	1002	1002
Thermoplastic Polyurethane (Melt Index 5-17 g/10 min. at 210°C, 3800 g. load)	--	10	20	50	100	100
Chlorinated Polyethylene	5	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5	5
Hardness - Shore A ASTM D-2240	67	67	72	71	73	73
Brittleness Temp. (°C) ASTM D-746	-21	-21.5	-25.5	-25.5	-28	-28
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	49,850	56,850	65,750	58,650	45,650	45,650
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	157	159	133	94	61	61
Tear Strength (PPI) ASTM D-624, die C	120	115	145	190	290	290

2Compound also contains - stabilizer and lubricant 5.5, co-stabilizer 3, filler 5, fire retardant and antioxidant 3.45, pigment and fungicide 16. Ingredients are added in parts per hundred resin unless otherwise indicated.

TABLE VIII

PVC/2-Ethylhexyl Acrylate Copolymer	100 ¹	100 ¹	100 ¹	100 ¹	100 ¹	100 ¹
Ethylene-Vinyl Acetate-Carbon Monoxide Terpolymer (Elvaloy 741) ³	--	10	20	50	100	100
Chlorinated Polyethylene	5	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5	5
Hardness - Shore A ASTM D-2240	73	78	77	74	73	73
Brittleness Temp. (°C) ASTM D-746	-17	-19	-19	-23	-23.5	-23.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	101,450	102,050	97,300	86,500	74,750	74,750
Oil Resistance - % Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	171	163	153	143	132	132
Tear Strength (PPI) ASTM D-624, die C	120	140	140	150	170	170

¹Compound also contains - stabilizer and lubricants 7.9, fire retardant and antioxidant 3.45, filler 35, pigment and fungicide 16. Ingredients added in parts per hundred resin unless otherwise indicated.

³E.I. DuPont de Nemours, Inc.

TABLE VIII (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	1002	1002	1002	1002	1002	1002
Ethylene-Vinyl Acetate-Carbon Monoxide Terpolymer (Elvaloy 741) ³	--	10	20	50	100	100
Chlorinated Polyethylene	5	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5	5
Hardness - Shore A ASTM D-2240	62	65	65	63	66	66
Brittleness Temp. (°C) ASTM D-746	-23	-26.5	-24	-29.5	-32	-32
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	52,450	53,550	56,150	55,200	54,400	54,400
Oil Resistance - % Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	183	174	166	149	137	137
Tear Strength (PPI) ASTM D-624, die C	95	105	105	115	135	135

²Compound also contains - stabilizer and lubricant 5.5, co-stabilizer 3, filler 5, fire retardant and antioxidant 3.45, pigment and fungicide 16. Ingredients are added in parts per hundred resin unless otherwise indicated.

³E.I. DuPont de Nemours, Inc.

TABLE IX

PVC/2-Ethylhexyl Acrylate Copolymer	1001	1001	1001	1001	1001	1001
Ethylene-Ethyl Acrylate Copolymer (6169NT, Union Carbide)	--	10	20	50	100	100
Chlorinated Polyethylene	5	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5	5
Hardness - Shore A ASTM D-2240	73	73	75	79	83	
Brittleness Temp. (°C) ASTM D-746	-15.5	-19.5	-20.5	-22	-26.5	
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	114,400	75,850	78,600	58,800	43,200	
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	165	268	271	208	*	
Tear Strength (PPI) ASTM D-624, die C	126	132	125	149	190	

* Compound also contains - stabilizer and lubricants 7.9, fire retardant and antioxidant 3.45, filler 35, pigment and fungicide 16. Ingredients are added in parts per hundred resin unless otherwise indicated.

* Sample disintegrated.

TABLE IX (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	1002	1002	1002	1002	1002
Ethylene-Ethyl Acrylate Copolymer (6169NT, Union Carbide)	--	10	20	50	100
Chlorinated Polyethylene	5	5	5	5	5
Phosphate Plasticizer	5	5	5	5	5
Hardness - Shore A ASTM D-2240	63	64	68	75	79
Brittleness Temp. (°C) ASTM D-746	-23	-24.5	-20	-24	-27.5
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	58,450	44,800	41,750	34,500	27,000
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	155	282	153	*	*
Tear Strength (PPI) ASTM D-624, die C	107	109	116	143	178

* Samples disintegrated.

2Compounds also contain - stabilizer and lubricant 5.5, co-stabilizer 3, filler 5, fire retardant and antioxidant 3.45, pigment and fungicide 16. Ingredients are added in parts per hundred resin unless otherwise indicated.

EXAMPLE 11

The blends listed in Tables X, XI, XII and XIII were prepared using a resin similar to that as described in Example 1. These blends were prepared on a heated 6" x 13" two-roll mill with a roll temperature of 160 to 191°C depending on the type and level of polymeric additive. The blends were removed from the mill as a sheet and cut into 6" x 6" plaques. These plaques were compression molded using a 5 minute preheat and

5 minute press cycle at 177° C. The molded specimens were then submitted for physical testing.

The results in Tables X, XI, XII and XIII indicate that products with significantly improved low temperature brittleness properties, improved tear strength and, depending on the polymer blending agent selected, reduced volume swell in hot oil, can be produced by blending thermoplastic rubbers with a polyvinyl chloride-acrylate copolymer.

TABLE XI

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100
Paraloid BTA 7332 (Methacrylate-Butadiene-Styrene Polymer)	-	20	50	100	200	300	400
Calcium Carbonate -3.5% Uncoated	-	-	-	-	-	-	-
Hardness - Shore A ASTM D-2240	61	69	76	80	85	85	85
Brittleness Temp. (OC) ASTM D-746	-22	-17.5	-41	-45.5	-48	-47.5	-47
Clash-Berg Modulus at -35OC (psi) ASTM D-1043	61,050	41,500	29,600	21,350	-	10,850	13,400
Oil Resistance - 0 Vol. Swell ASTM D-471, ASTM D3 Oil 100OC/166 Hrs.	180	175	166	165	144	145	158
Tear Strength (PPI) ASTM D-624, die C	107	119	130	162	140	135	140

1 Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

2 Rohm and Haas, Inc.

TABLE X¹ (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100	100
Paraloid BTA 7332 (Methacrylate-Butadiene-Styrene Polymer)	-	20	50	100	200	300	400		
Calcium Carbonate -3.5% Uncoated	20	20	20	20	20	20	20	20	20
Hardness - Shore A ASTM D-2240	67	73	78	82	85	85	86		
Brittleness Temp. (°C) ASTM D-746	-25	-30.5	-41	-47	-46.5	-49.5	-47.5		
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	68,300	53,550	38,650	23,200	17,550	12,350	16,250		
Oil Resistance - 0 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	160	160	166	164	143	136	146		
Tear Strength (PPI) ASTM D-624, die C	97	107	115	142	140	135	145		

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

2Rohm and Haas, Inc.

TABLE XI¹

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100
Blendex 3382 (Acrylonitrile-Butadiene-Styrene Polymer)	-	20	50	100	200	300	400	
Calcium Carbonate -3.5% Uncoated	-	-	-	-	-	-	-	-
Hardness - Shore A ASTM D-2240	61	69	76	83	86	88	90	
Brittleness Temp. (°C) ASTM D-746	-22	-10	-15	-51.5	-76	*	*	*
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	61,050	47,900	27,500	20,150	*	*	*	*
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	180	170	175	185	187	185	181	
Tear Strength (PPI) ASTM D-624, die C	107	122	144	161	165	180	200	

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

²General Electric, Inc.

*Value was too low to be recorded by test apparatus.

TABLE XI¹ (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100
Blendex 3382 (Acrylonitrile-Butadiene-Styrene Polymer)	-	20	50	100	200	300	400
Calcium Carbonate - 3.5% Uncoated	20	20	20	20	20	20	20
Hardness - Shore A ASTM D-2240	67	74	78	83	87	90	89
Brittleness Temp. (°C) ASTM D-746	-25	-11	-17	-50.5	*	*	*
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	68,300	54,800	38,300	19,700	*	*	*
Oil Resistance - % Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	160	176	180	181	185	182	181
Tear Strength (PPI) ASTM D-624, die C	97	119	139	157	175	190	195

Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

2General Electric, Inc.

*Value was too low to be recorded by test apparatus.

TABLE XII¹

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100	100	100
Durastrength 2002 (Acrylic Polymer)	-	20	50	100	200	300	400			
Calcium Carbonate -3.5% Uncoated	-	-	-	-	-	-	-	-	-	-
Hardness - Shore A ASTM D-2240	61	69	76	83	89	91	91			
Brittleness Temp. (°C) ASTM D-746	-22	-18	-21	-27	-36.5	-41.5	-43.5			
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	61,050	47,700	34,850	32,800	39,450	33,500	17,350			
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	180	165	149	132	112	103	97			
Tear Strength (PPI) ASTM D-624, die C	107	127	137	163	160	175	175			

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

2M & T Chemicals, Inc.

TABLE XII¹ (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100	100
Durastrength 2002 (Acrylic Polymer)	-	20	50	100	200	300	400		
Calcium Carbonate - 3.5% Uncoated	20	20	20	20	20	20	20	20	20
Hardness - Shore A ASTM D-2240	67	72	77	84	89	91	91		
Brittleness Temp. (°C) ASTM D-746	-25	-26	-32	-37.5	-40.5	-44	-45		
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	68,300	58,000	42,300	31,850	50,000	19,550	17,750		
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM D-3 Oil 100°C/166 Hrs.	160	155	138	125	109	102	97		
Tear Strength (PPI) ASTM D-624, die C	97	115	126	151	165	185	185		

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

2M & T Chemicals, Inc.

TABLE XIII¹

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100	100
Paraloid KM-334 (Acrylic Polymer) ²	-	20	50	100	200	300	400		
Calcium Carbonate -3.5/4 Uncoated	-	-	-	-	-	-	-	-	-
Hardness - Shore A ASTM D-2240	61	72	80	84	88	90	90		
Brittleness Temp. (°C) ASTM D-746	-22	-21.5	-32	-39.5	-45	-47.5	-51.5		
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	61,050	49,850	43,900	33,750	23,650	22,100	18,750		
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM #3 Oil 100°C/166 Hrs.	180	160	132	115	97	91	84		
Tear Strength (PPI) ASTM D-624, die C	107	132	150	169	165	180	170		

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

²Rohm and Haas, Inc.

TABLE XIII¹ (Con't)

PVC/2-Ethylhexyl Acrylate Copolymer	100	100	100	100	100	100	100	100	100
Paraloid KM-334 (Acrylic Polymer) ²	-	20	50	100	200	300	400		
Calcium Carbonate - 3.5% Uncoated	20	20	20	20	20	20	20	20	20
Hardness - Shore A ASTM D-2240	67	75	82	87	90	90	89		
Brittleness Temp. (°C) ASTM D-746	-25	-27	-33.5	-37	-44	-45.5	-44		
Clash-Berg Modulus at -35°C (psi) ASTM D-1043	68,300	55,600	48,400	39,950	25,450	22,400	19,300		
Oil Resistance - 1 Vol. Swell ASTM D-471, ASTM D-3 Oil 100°C/166 Hrs.	160	153	126	112	95	90	86		
Tear Strength (PPI) ASTM D-624, die C	97	125	138	163	175	180	180		

¹Compounds also contain - stabilizer 3, co-stabilizer 4, lubricant and antioxidant 1.0. Ingredients are added in parts per hundred resin unless otherwise indicated.

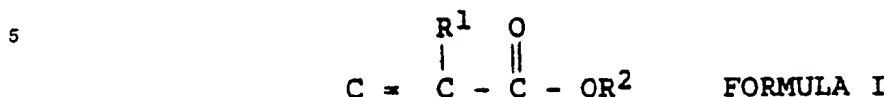
²Rohm and Haas, Inc.

While in accordance with the Patent Statutes, the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

Claims

- 1: A soft, flexible polyvinyl chloride composition, comprising:
a polyvinyl chloride-acrylate copolymer, said polyvinyl chloride-acrylate copolymer containing from (a) about 10 parts to about 90 parts by weight of vinyl chloride units and optional vinyl component units wherein the amount of said optional vinyl component units is from about 0 to about 45 parts by weight and

from (b) about 90 parts to about 10 parts by weight of one or more acrylate units, said acrylate unit, before polymerization, having the formula

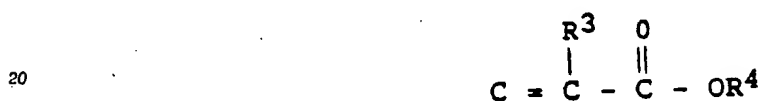


wherein R¹ is an aromatic, an aliphatic, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative thereof, or hydrogen, and wherein R² is an aliphatic, an aromatic, an alkyl hydroxyl, or combinations thereof having from 1 to 18 carbon atoms, or a halogen derivative thereof; or a hydrocarbyl ether including an alkoxyalkyl, a phenoxyaryl, a phenoxyalkyl, or combinations thereof, having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, sulfur, or nitrogen derivative thereof, and from about 0 parts to about 300 parts by weight of a plasticizer.

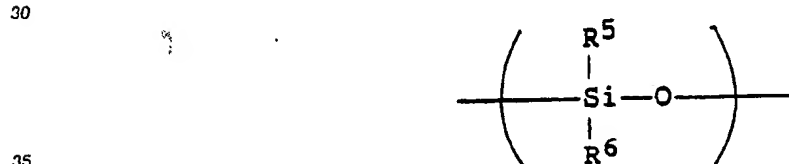
2. A soft, flexible polyvinyl chloride composition according to Claim 1, wherein said plasticizer is an adipic acid derivative, an azelaic acid derivative, a benzoic acid derivative, a citric acid derivative, an epoxy derivative, an ether, a formal, a glycol derivative, a glycolate, a glycerol derivative, a polyglycerol derivative, a petroleum derivative, an isobutyric acid derivative, an isophthalic acid derivative, an isosebacic acid derivative, an oleic acid derivative, a paraffin, a pentaerythritol derivative, a phosphoric acid derivative, a phthalic acid derivative, a ricinoleic acid derivative, a sebacic acid derivative, a stearic acid derivative, a sulfonamide, a sulfonate, a tartaric acid derivative, a terephthalate, a trimellitate, mineral oil, a polyester, a polystyrene or a derivative thereof, a nitrile-butadiene copolymer, a chlorinated polyolefin made from a monomer having from 1 to 18 carbon atoms, an oxidized polyolefin made from a monomer having from 1 to 18 carbon atoms, polyepichlorohydrin or a copolymer thereof, a polyacrylate, a polysiloxane, and combinations of the above plasticizers, wherein the amount of said vinyl chloride and said optional vinyl component units is from about 20 parts to about 80 parts by weight, wherein the amount of said optional vinyl component units is from about 0 to about 20 parts by weight, wherein said optional vinyl component unit, before polymerization, is a vinyl ester having from 1 to 18 carbon atoms in the ester portion, vinylidene chloride, 1,2-dichloroethylene, styrene or a styrene derivative having a total of from 8 to 15 carbon atoms, vinyl naphthalene, a diolefin having a total of from 4 to 18 carbon atoms, or a monoolefin having a total of from 2 to 18 carbon atoms, wherein the amount of said one or more acrylate units of said polyvinyl chloride-acrylate copolymer is from about 80 parts to about 20 parts by weight.

3. A soft, flexible polyvinyl chloride composition according to Claim 2, wherein said adipic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said azelaic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said benzoic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms, wherein said citric acid derivative is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said ether has a total of from about 2 to about 50 carbon atoms, wherein said formal has a total of from about 3 to about 40 carbon atoms, wherein said glycol derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms, wherein said glycolate derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 20 carbon atoms, wherein said glycerol derivative and said polyglycerol derivative is an ester wherein each acid group which forms the ester, independently, contains from 1 to 18 carbon atoms, wherein said isobutyric acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said isophthalic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said isosebacic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said oleic acid derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said paraffin is chlorinated paraffin, wherein said pentaerythritol derivative is an ester wherein each acid group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said phosphoric acid derivative is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said phthalic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said ricinoleic acid derivative is an

ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said sebacic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said stearic acid derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said tartaric acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said terephthalate is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said trimellitate is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, mineral oil, wherein said styrene derivative is made from styrene or styrene derivatives having from 8 to 12 carbon atoms, wherein said polyester is made from a dicarboxylic acid having from 2 to about 12 carbon atoms, and a diol having from about 2 to about 1,000 carbon atoms, wherein said nitrile-butadiene copolymer has a nitrile content of 50 percent or less by weight, wherein said chlorinated polyolefin contains 50 percent or less by weight of chlorine therein, wherein said polyepichlorohydrin polymer or said copolymer has a weight average molecular weight of from about 100,000 to about 1,000,000, and wherein said polyacrylate forming monomers have the formula



wherein R^3 is an aromatic, an aliphatic, or combinations thereof having from 1 to 18 carbon atoms, or hydrogen, or a halogen derivative thereof, and R^4 is an aliphatic such as an alkyl, an aromatic, an alkyl hydroxyl, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative of the above; or a hydrocarbyl ether having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, nitrogen, or sulfur derivative thereof, wherein said polysiloxane has repeat units of the formula



where R^5 and R^6 , independently, is an aliphatic or an aromatic having from 1 to 18 carbon atoms, or combinations of the above plasticizers.

4. A soft, flexible polyvinyl chloride composition according to Claim 3, wherein said R^1 is methyl or hydrogen, wherein R^2 is an alkyl having from 2 to 10 carbon atoms, or an alkoxyalkyl, a phenoxyaryl, or a phenoxyalkyl, having from 2 to 18 carbon atoms, or combinations thereof, and wherein the amount of said plasticizer is from about 2 parts to about 100 parts by weight per 100 parts by weight of said polyvinyl chloride-acrylate copolymer.

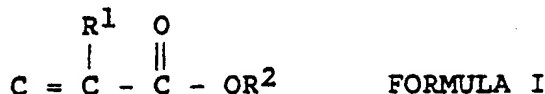
5. A soft, flexible polyvinyl chloride composition according to Claim 4, wherein said optional vinyl component unit, before polymerization, is vinyl acetate, wherein the amount of said vinyl chloride and said optional vinyl acetate units is from about 30 to about 60 parts by weight, and wherein the amount of said one or more acrylate units forming said polyvinyl chloride-acrylate copolymer is from about 70 parts to about 40 parts by weight, wherein R^1 is hydrogen, wherein R^2 is an alkyl having from 2 to 8 carbon atoms, and wherein the amount of said plasticizer is from about 5 parts to about 50 parts by weight per 100 parts by weight of said polyvinyl chloride-acrylate copolymer.

6. A soft, flexible polyvinyl chloride composition according to Claim 5, wherein said plasticizer is diisobutyl adipate, di-2-ethylhexyl adipate, heptyl nonyl adipate, octyl decyl adipate, diisodecyl adipate, dibutoxyethyl adipate, di(methylcyclohexyl) adipate, bis(2,2,4-trimethyl-1,3-pentenediolmono isobutyrate) adipate, dibutyl phthalate, diisohexyl phthalate, dimethylisobutylcarbonyl phthalate, butyl octyl phthalate, butyl isodecyl phthalate, di-n-octyl phthalate, di-2-ethylhexyl phthalate, diisooctyl phthalate, dicapryl phthalate, di(heptyl,nonyl) phthalate, di(heptyl,nonyl, undecyl) phthalate, diisononyl phthalate, n-octyl n-decyl phthalate, diisodecyl phthalate, diundecyl phthalate, ditridecyl phthalate, diallyl phthalate,

dihydroabietyl phthalate, butyl cyclohexyl phthalate, butyl benzyl phthalate, alkyl benzyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, alkyl aryl modified phthalate, dimethoxyethyl phthalate, diethoxyethoxyethyl phthalate, dibutoxyethyl phthalate, tri-2-ethylhexyl trimellitate, tri(heptyl,nonyl)trimellitate, n-octyl, n-decyl trimellitate, triisodecyl trimellitate, tri-n-octyl trimellitate, adipate based polyester, glutarate based polyester, tri-2-ethylhexyl trimellitate, mineral oil, dibutoxyethoxyethyl formal, wherein said nitrile-butadiene copolymer has a nitrile content of 40 percent by weight or less, mineral oil, dibutoxyethoxyethyl formal, or said polyesters, or said polysiloxane wherein R⁵ and R⁶ of said repeat unit, independently, is methyl or phenyl, or combinations of the above plasticizers.

7. A soft, flexible polyvinyl chloride composition, comprising:
 10 a polyvinyl chloride-acrylate copolymer, said copolymer containing from (a) about 10 parts to about 90 parts by weight of vinyl chloride units and optional vinyl component units wherein the amount of said optional vinyl component units is from about 0 to about 45 parts by weight and from (b) about 90 parts to about 10 parts by weight of one or more acrylate units, said acrylate unit, before polymerization, having the formula

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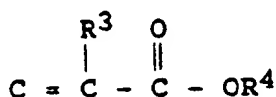
wherein R¹ is an aromatic, an aliphatic, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative thereof, or hydrogen, and wherein R² is an aliphatic, an aromatic, an alkyl hydroxyl, or combinations thereof having from 1 to 18 carbon atoms, or a halogen derivative thereof; or a hydrocarbyl ether including an alkoxyalkyl, a phenoxyaryl, a phenoxyalkyl, or combinations thereof, having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, sulfur, or nitrogen derivative thereof, and
 25 an effective amount of a plasticizer so that said plasticized polyvinyl chloride-acrylate copolymer composition has a Shore A hardness of 55 or less.

8. A soft, flexible polyvinyl chloride composition according to Claim 7, wherein said Plasticizer is an adipic acid derivative, an azelaic acid derivative, a benzoic acid derivative, a citric acid derivative, an epoxy derivative, an ether, a formal, a glycol derivative, a glycolate, a glycerol derivative, a polyglycerol derivative, a petroleum derivative, an isobutyric acid derivative, an isophthalic acid derivative, an isosebacic acid derivative, an oleic acid derivative, a paraffin, a pentaerythritol derivative, a ricinoleic acid derivative, a sebacic acid derivative, a stearic acid derivative, a sulfonamide, a sulfonate, a tartaric acid derivative, a terephthalate, a trimellitate, mineral oil, a polyester, a polystyrene or a derivative thereof, a nitrile-butadiene copolymer, a chlorinated polyolefin made from a monomer having from 1 to 18 carbon atoms, an oxidized polyolefin made from a monomer having from 1 to 18 carbon atoms, polyepichlorohydrin or a copolymer thereof, polyacrylate, a polysiloxane, and combinations of the above plasticizers.

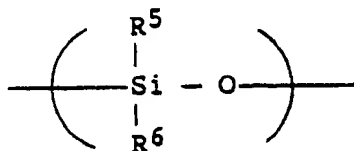
9. A soft, flexible polyvinyl chloride composition according to Claim 8, wherein the amount of said vinyl chloride and said optional vinyl component units is from about 20 parts to about 80 parts by weight, wherein the amount of said optional vinyl component units is from about 0 to about 20 parts by weight, wherein said optional vinyl component unit, before polymerization, is a vinyl ester having from 1 to 18 carbon atoms in the ester portion, vinylidene chloride, 1,2-dichloroethylene, styrene or a styrene derivative having a total of from 8 to 15 carbon atoms, vinyl naphthalene, a diolefin having a total of from 4 to 18 carbon atoms, or a monoolefin having a total of from 2 to 18 carbon atoms, wherein the amount of said one or more acrylate units of said polyvinyl chloride-acrylate copolymer is from about 80 parts to about 20 parts by weight, and
 45 wherein said effective amount of said polyvinyl chloride plasticizer is such that said plasticized polyvinyl chloride-acrylate copolymer composition has a Shore A hardness of 50 or less.

10. A soft, flexible polyvinyl chloride composition according to Claim 9, wherein said adipic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said azelaic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said benzoic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms, wherein said citric acid derivative is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said ether has a total of from about 2 to about 50 carbon atoms, wherein said formal has a total of from about 3 to about 40 carbon atoms, wherein said glycol derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 100 carbon atoms, wherein said glycolate derivative is an ester wherein each alcohol group which forms the ester, independently, contains

from about 1 to about 20 carbon atoms, wherein said glycerol derivative and said polyglycerol derivative is an ester wherein each acid group which forms the ester, independently, contains from 1 to 18 carbon atoms, wherein said isobutyric acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said isophthalic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said isosebacic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said oleic acid derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said paraffin is chlorinated paraffin, wherein said pentaerythritol derivative is an ester wherein each acid group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said phosphoric acid derivative is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said phthalic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said ricinoleic acid derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said sebacic acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said stearic acid derivative is an ester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said tartaric acid derivative is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said terephthalate is a diester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, wherein said trimellitate is a triester wherein each alcohol group which forms the ester, independently, contains from about 1 to about 18 carbon atoms, mineral oil, wherein said styrene derivative is made from styrene or styrene derivatives having from 8 to 12 carbon atoms, wherein said polyester is made from a dicarboxylic acid having from 2 to about 12 carbon atoms, and a diol having from about 2 to about 1,000 carbon atoms, wherein said nitrile-butadiene copolymer has a nitrile content of 50 percent or less by weight, wherein said chlorinated polyolefin contains 50 percent or less by weight of chlorine therein, wherein said polyepichlorohydrin polymer or said copolymer has a weight average molecular weight of from about 100,000 to about 1,000,000, and wherein said polyacrylate forming monomers have the formula



wherein R^3 is an aromatic, an aliphatic, or combinations thereof having from 1 to 18 carbon atoms, or hydrogen, or a halogen derivative thereof, and R^4 is an aliphatic such as an alkyl, an aromatic, an alkyl hydroxyl, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative of the above; or a hydrocarbonyl ether having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, nitrogen, or sulfur derivative thereof, wherein said polysiloxane has repeat units of the formula



where R^5 and R^6 , independently, is an aliphatic or an aromatic having from 1 to 18 carbon atoms, or combinations of the above plasticizers.

11. A soft, flexible polyvinyl chloride composition according to Claim 10, wherein said optional vinyl component unit, before polymerization, is vinyl acetate, wherein the amount of said vinyl chloride and said optional vinyl acetate units is from about 30 to about 60 parts by weight, and wherein the amount of said one or more acrylate units forming said polyvinyl chloride-acrylate copolymer is from about 70 parts to about 40 parts by weight, wherein said plasticizer is said diisobutyl adipate, di-2-ethylhexyl adipate, heptyl

nonyl adipate, octyl decyl adipate, diisodecyl adipate, dibutoxyethyl adipate, di(methylcyclohexyl) adipate, bis(2,2,4-trimethyl-1,3-pentanediolmono isobutyrate) adipate, dibutyl phthalate, diisohexyl phthalate, dimethylisobutylcarbonyl phthalate, butyl octyl phthalate, butyl isodecyl phthalate, di-n-octyl phthalate, di-2-ethylhexyl phthalate, diisooctyl phthalate, dicapryl phthalate, di(heptyl,nonyl) phthalate, di(heptyl,nonyl, undecyl) phthalate, diisononyl phthalate, n-octyl n-decyl phthalate, diisodecyl phthalate, diundecyl phthalate, ditridecyl phthalate, diallyl phthalate, dihydroabietyl phthalate, butyl cyclohexyl phthalate, butyl benzyl phthalate, alkyl benzyl phthalate, dicyclohexyl phthalate, diphenyl phthalate, alkyl aryl modified phthalate, dimethoxyethyl phthalate, diethoxyethoxyethyl phthalate, dibutoxyethyl phthalate, tri-2-ethylhexyl trimellitate, tri(heptyl,nonyl)trimellitate, n-octyl, n-decyl trimellitate, triisodecyl trimellitate, tri-n-octyl trimellitate, wherein said nitrile-butadiene copolymer has a nitrile content of 40 percent by weight or less, mineral oil, dibutoxyethoxyethyl formal, or said polyesters, or said polysiloxane wherein R⁵ and R⁶ of said repeat unit, independently, is methyl or phenyl, or combinations of the above plasticizers.

12. A soft, flexible polyvinyl chloride composition according to Claim 11, wherein said plasticizer is di-2-ethylhexyl phthalate, di-2-ethylhexyl adipate, an adipate based polyester, a glutarate based polyester, tri-2-ethylhexyl trimellitate, diisodecyl phthalate, ditridecyl phthalate, mineral oil, dibutoxyethoxyethyl formal, or said polysiloxane, wherein R⁵ and R⁶ of said repeat unit, independently, is methyl or phenyl, or combinations of the above plasticizers.

13. A soft, flexible polyvinyl chloride composition according to Claim 9, Claim 11 or Claim 12 wherein said effective amount of said plasticizer is such that said polyvinyl chloride-acrylate copolymer composition has a Shore A hardness of 40 or less.

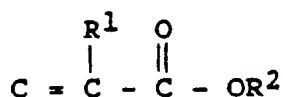
14. A soft, flexible polyvinyl chloride composition according to Claim 7, wherein said composition has an ASTM D-746 brittleness temperature of minus 35° C or less and has a Clash-Berg low temperature modulus at minus 35° C of 50,000 psi or less.

15. A soft, flexible polyvinyl chloride composition according to Claim 10, wherein said composition has an ASTM D-746 brittleness temperature of minus 40° C or less, and has a Clash-Berg low temperature modulus at minus 35° C of 20,000 psi or less.

16. A soft, flexible polyvinyl chloride composition according to Claim 1, wherein said composition is free of a plasticizer, and wherein R¹ is methyl or hydrogen, wherein R² is an alkyl having from 2 to 10 carbon atoms, or an alkoxyalkyl, or a phenoxyaryl, or a phenoxyalkyl, having from 2 to 18 carbon atoms, or combinations thereof.

17. A soft, flexible polyvinyl chloride composition according to Claim 16, wherein said optional vinyl component unit, before polymerization, is vinyl acetate, wherein the amount of said vinyl chloride and said optional vinyl acetate units is from about 40 to about 60 parts by weight, wherein the amount of said one or more acrylate units forming said polyvinyl chloride-acrylate copolymer is from about 60 parts to about 40 parts by weight, wherein R¹ is hydrogen, and wherein R² is an alkyl having from 2 to 8 carbon atoms.

18. A soft, flexible polyvinyl chloride composition, comprising:
a polyvinyl chloride-acrylate copolymer, said copolymer made containing from (a) about 10 parts to about 90 parts by weight of vinyl chloride units and optional vinyl component units wherein the amount of said optional vinyl component units is from about 0 to about 45 parts by weight and from (b) about 90 parts to about 10 parts by weight of one or more acrylate units, said acrylate unit, before Polymerization, having the formula



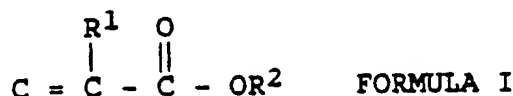
FORMULA I

wherein R¹ is an aromatic, an aliphatic, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative thereof, or hydrogen, and wherein R² is an aliphatic, an aromatic, an alkyl hydroxyl, or combinations thereof having from 1 to 18 carbon atoms, or a halogen derivative thereof; or a hydrocarbyl ether including an alkoxyalkyl, a phenoxyaryl, a phenoxyalkyl, or combinations thereof, having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, sulfur, or nitrogen derivative thereof, said polyvinyl chloride-acrylate copolymer being free of a plasticizer.

19. A soft, flexible polyvinyl chloride composition according to Claim 18, wherein the amount of said vinyl chloride and said optional vinyl component units is up to 55 parts by weight, wherein the amount of said optional vinyl component units is from about 0 to about 20 parts by weight, wherein said optional vinyl component unit, before polymerization, is a vinyl ester having from 1 to 18 carbon atoms in the ester

portion, vinylidene chloride, 1,2-dichloroethylene, styrene or a styrene derivative having a total of from 8 to 15 carbon atoms, vinyl naphthalene, a diolefin having a total of from 4 to 18 carbon atoms, or a monoolefin having a total of from 2 to 18 carbon atoms, wherein the amount of said one or more acrylate units of said polyvinyl chloride-acrylate copolymer is at least 45 parts by weight and wherein said composition has a Shore A hardness of 55 or less.

20. A composition according to claim 1 having favorable low temperature properties, comprising: a polyvinyl chloride-acrylate copolymer, said polyvinyl chloride-acrylate copolymer containing from (a) about 10 parts to about 90 parts by weight of vinyl chloride units and optional vinyl component units wherein the amount of said optional vinyl component units is from about 0 to about 45 parts by weight and from (b) about 90 parts to about 10 parts by weight of one or more acrylate units, said acrylate unit, before polymerization, having the formula



wherein R¹ is an aromatic, an aliphatic, or combinations thereof, having from 1 to 18 carbon atoms, or a halogen derivative thereof, or hydrogen, and wherein R² is an aliphatic, an aromatic, an alkyl hydroxyl, or combinations thereof having from 1 to 18 carbon atoms, or a halogen derivative thereof; or a hydrocarbyl ether including an alkoxyalkyl, a phenoxyaryl, a phenoxyalkyl, or combinations thereof, having from 2 to 1,000 carbon atoms, or a substituted halogen, oxygen, sulfur, or nitrogen derivative thereof; and said polyvinyl chloride-acrylate copolymer further being blended with one or more low temperature property improving polymers, said composition having a low temperature brittleness of less than -10° C as measured by ASTM D-746.

21. A composition according to Claim 20, wherein the low temperature brittleness is at least -30° C.

22. A composition according to Claim 20, wherein said low temperature property improving polymer is one or more polymers selected from the group consisting of polyester elastomers, thermoplastic polyurethanes, thermoplastic rubbers or elastomers, and ethylene polymers; wherein said composition has a tear resistance of greater than about 30 lbs/in as measured by ASTM D-624, using die C and has an oil swell of from 0 percent to about 300 percent, as measured in hot ASTM #3 oil at 100° C for 166 hours.

23. A composition according to Claim 20, wherein the low temperature improving polymer comprises a polyester elastomer, which has a weight average molecular weight of greater than 5,000, wherein said polyester elastomer has a Shore D hardness, ASTM D-2240, of less than about 50.

24. A composition according to Claim 20, wherein the low temperature property improving polymer comprises a thermoplastic polyurethane made from a polyester or a polyether polyol intermediate, said polyurethane having a weight average molecular weight greater than 5,000; said intermediate is reacted with a polyisocyanate having a formula (RNCO)_n, wherein R is an aliphatic or aromatic or combinations thereof, and the subscript "n" is an integer from 2 to 4; and wherein said polyurethane has a Shore D hardness, ASTM D2240, of less than about 50.

25. A composition according to Claim 20, wherein the low temperature property improving polymer comprises a rubber having a weight average molecular weight of more than 15,000 and is selected from the group consisting of natural rubber; ethylene-propylene rubber; derivatives of polyethylene; ethylene-propylene-diene rubber; rubbers made from conjugated dienes having from 4 to 12 carbon atoms; butyl and halogenated butyl elastomers; silicone elastomers; fluorocarbon elastomers; rubbers made from vinyl substituted aromatics having from 8 to 12 carbon atoms; elastomers prepared from halogenated diolefins; thermoplastic elastomers; and block or graft copolymers; and overpolymers.

26. A composition according to Claim 25, wherein said rubber is selected from the group consisting of styrene conjugated diene block copolymers or derivatives thereof and dynamically vulcanized thermoplastic elastomers, and polyolefin thermoplastic elastomers.

27. A composition according to Claim 25, wherein said rubber is prepared from one or more of the monomers consisting of acrylonitrile, methylmethacrylate, styrene, methyl acrylate, butadiene, ethyl acrylate, and butyl acrylate, said monomer being overpolymerized unto one or more of the group consisting of elastomers prepared from butadiene, acrylates and chlorinated polyolefins.

28. A composition according to Claim 20, wherein said low temperature property polymer, comprises a polymer having a weight average molecular weight in excess of 100,000 and is selected from the group comprising copolymers of ethylene with one or more of (1) vinyl esters having from 1 to 18 carbon atoms in

the acid portion used to make the ester (2) acrylates, wherein the acrylate has from 1 to 18 carbon atoms in the alcohol portion used to make the acrylate; and (3) monoolefins having from 2 to 18 carbon atoms; and (4) carbon monoxide.

29. A composition according to Claim 28, wherein said ethylene copolymer is a copolymer of ethylene
 5 with one or more of (1) vinyl acetate; (2) acrylate, wherein the alcohol portion used to make the acrylate has from 1 to 4 carbon atoms; (3) monoolefins having from 2 to 8 carbon atoms; and (4) carbon monoxide.

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Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 358 181 A3

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **89116424.6**(51) Int. Cl.⁵: **C08L 27/06, C08L 33/00**(22) Date of filing: **06.09.89**

(30) Priority: **09.09.88 US 242394**
17.03.89 US 342800

(43) Date of publication of application:
14.03.90 Bulletin 90/11

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(88) Date of deferred publication of the search report:
04.09.91 Bulletin 91/36

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(54) **Polyvinyl chloride blends having improved physical properties.**

(57) Polyvinyl chloride-acrylate copolymers are plasticized with plasticizers to produce a composition having low hardness values. For example, Shore A values of 55 or less can be readily achieved. Such low values are often achieved by utilizing low amounts, for example less than 100 parts by weight, of the plasticizer for every 100 parts by weight of the PVC-acrylate copolymer. Low Shore A hardness values are also aided by the use of high amounts of acrylate units in the copolymer, that is amounts of at least 45 percent by weight based upon the total weight of the copolymer. The copolymer is made from a vinyl constituent which is a vinyl chloride monomer with an optional vinyl component comonomer and one or more acrylate monomers.

EP 0 358 181 A3



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EUROPEAN SEARCH REPORT

Application Number

EP 89 11 6424

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 7, no. 53 (C-154)(1198) 3 March 1983, & JP-A-57 200435 (NIPPON ZEON KK) 8 December 1982, * the whole document *	1,4,18	C 08 L 27/06 C 08 L 33/00
X	US-A-3 167 533 (DONAT) * column 9, lines 35 - 50 * * example III *	1-3,18-19	
X	C.A. Brighton: "Encyclopedia of Polymer Science and Technology Vol. 14" 1971, Interscience, New York * pages 353 - 355; figure 5 *	1-3,18-19	
X	DE-A-1 595 428 (CHISSO CORP) * page 8, line 17 - page 9, line 9 *	1-4	
X	EP-A-0 169 451 (HOECHST AG) * page 4, lines 8 - 30 *	1-3	
X	US-A-2 889 308 (FEDDERSON) * column 5, line 64 - column 6, line 26 *	1-4,7-10	
X	BE-A-6 040 28 (SOLVAY & CIE) * page 2, line 6 *	1-4	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	FR-A-1 584 895 (PRODUITS CHIMIQUES PECHINEY- SAINT-GOBAIN) * page 2, lines 12 - 39 *	1	C 08 L C 08 K C 08 F
X	Plaste und Kautschuk vol. 20, no. 10, 1973, Berlin (DDR) pages 728 - 737; A.A. Berlin: "Polymer-Oligomer-Kompositionen und Materialien auf ihrer Grundlage" * figures 18, 20 *	1-4	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		10 July 91	SCHUELER D.H.H.
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